Thermodynamics of Means

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Thermodynamics of power means applies to an ideal quantum gas which may be nonextensive. Transition to an ideal classical gas occurs when the empirical temperature exponents of the internal energy and absolute temperature coalesce. Limiting processes are pure heat conduction and pure deformations. Largest and smallest mean final volumes occur for isothermal and adiabatic processes, respectively. The increment in the heat admits two integrating factors which yield conserved quantities for adiabatic processes. Energy-conserving equilibrations yield the largest final means possible, while the second law follows from the property that the power means are monotonically increasing functions of their order. In the ideal classical gas limit, the change in the average entropy is proportional to the difference between the Shannon and Rényi entropies for nonextensive, isothermal systems that are multifractal in nature.

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Thermodynamics developed largely independently of all the classical branches of mathematics. Unlike other laws of physics, the second law is an inequality, whose generality rests on there not being macroscopic violations of that inequality. Inequalities is a well-established branch of mathematics [1], and it would be of interest to show that the laws of thermodynamics can be derived from well-known inequalities.

Carathéodory's formulation of the second law, in its most general nonstatical form [2], states that in every neighborhood of any given state, there exists adiabatically inaccessible states even when nonstatical processes are permitted. If we envision an entropy change, ΔS , in which dQ=0 (adiabatic), and at constant volume, the entropy of the system can only increase or decrease. Since this is true no matter what the initial state is, it must be always increase or always decrease. In order to determine which of the two possibilities is the correct one, recourse must be made to experiment—albeit a single experiment suffices.

It would be more gratifying if the entropy change could be determined by a mathematical inequality, that would be independent of any particular process or type of substance considered. In a little known paper, Cashwell and Everett [3] do just this without exploiting the full impact of their findings. What they do is to show that the final mean temperature of order-q in an energy-conserving equilibration is necessarily greater than the mean of order-(q - r), where q > r, of an entropy-conserving equilibration. Thus, the increase in entropy is due to the property that power means are increasing functions of their order [4].

In a series of papers, Landsberg [5], and Landsberg and Pečarič [6], rediscover the Cashwell-Everett results in the case of constant, but not necessarily positive, heat

capacities. Both Cashwell-Everett and Landsberg were anteceded by Sommerfeld [7] who derived the arithmetic-geometric mean inequality for the temperature from the second law as an exercise. Sidhu [8] generalized Landsberg's result to arbitrary power means of order-q>1, or, equivalently, to systems whose heat capacities are some positive power of the temperature. Negative orders were excluded on the basis that it would contradict the third law of thermodynamics.

From a mathematical viewpoint, there is no qualitative distinction between the arithmetic mean, q=1, and power means, q>1. However, there is a thermodynamic distinction insofar as the former applies to an ideal *classical* gas (ICG), while the later to an ideal *quantum* gas (IQG).

Our starting point will be the purely mechanical equation of state [9, 10]

$$pV = \frac{r}{q - r}U,\tag{1}$$

which we will assume to hold for IQG, although a formally analogous relation will appear for ICG, where p is the pressure, V the volume of the container, and U the internal energy. r and q are positive rational numbers, where q>r.

Differentiating (1) with respect to V, at a constant empirical temperature t, and using a combination of the Gibbs equation and a Maxwell relation result in

$$\begin{split} V\left(\frac{\partial p}{\partial V}\right)_t + p &= \frac{r}{q-r}\left(\frac{\partial U}{\partial V}\right)_t \\ &= \frac{1}{q-r}\left\{t\left(\frac{\partial p}{\partial t}\right)_V - rp\right\}. \end{split}$$

This partial differential equation has the general solution

$$p = \frac{r}{q-r} V^{-q/(q-r)} Z(z),$$

or, equivalently,

$$U = V^{-r/(q-r)}Z(z), \tag{2}$$

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on the strength of (1), where $z = tV^{1/(q-r)}$.

At this point we can impose the property of homogeneity of the internal energy by requiring

$$\left(\frac{\partial p}{\partial V}\right)_t = 0,\tag{3}$$

which, in view of (1), implies that U is first-order homogeneous. It will be appreciated that (3) is a condition for phase equilibrium. Varying the volume at constant temperature leaves the vapor pressure constant by having the liquid evaporate or the vapor condense. This fine balance keeps the pressure constant and preserves the homogeneity of the internal energy. Moreover, it determines $Z=z^q$, where we take the constant of proportionality equal to unity for simplicity sake. The condition of first-order homogeneity is, however, not necessary.

From (2) we can write

$$UV^{r/(q-r)} = z^{\alpha} = t^{\alpha}V^{\alpha/(q-r)} =: Z(z), \tag{4}$$

by assuming a power expression for Z(z). The particular choice, $q = \alpha$, renders the internal energy homogeneous, and the system extensive.

Solving for U,

$$U = t^{\alpha} V^{(\alpha - r)/(q - r)}, \tag{5}$$

and using (1) give

$$p = \frac{r}{q - r} t^{\alpha} V^{(\alpha - q)/(q - r)}.$$
 (6)

The analogy with the Joule-Thomson effect will help clarify the role of the exponents. The condition that the entropy be an exact differential is

$$\left(\frac{\partial H}{\partial p}\right)_t = V - \frac{t}{r} \left(\frac{\partial V}{\partial t}\right)_p =: C_p \mu, \tag{7}$$

where H is the enthalphy [cf. (14) below], and C_p is the heat capacity at constant pressure. Using (6), we evaluate the Joule-Thomson coefficient, μ , as

$$\mu C_p = \frac{q}{r} \left(\frac{\alpha - r}{\alpha - q} \right) V, \tag{8}$$

since

$$\left(\frac{\partial V}{\partial t}\right)_{p} = -\frac{V}{t} \left(\frac{q-r}{\alpha-q}\right). \tag{9}$$

When $\alpha > q$, μ is positive and there is a cooling effect. Alternatively, when $q > \alpha > r$, μ is negative and there is a heating effect. When the system is extensive, $\alpha = q$, (8) implies that $C_p = \infty$. The inversion point occurs when $\alpha = r$. For an extensive system, (3) shows that the pressure depends only on the temperature, and is independent of the volume. Since constant pressure implies constant temperature, when heat is added to the system

the temperature must remain fixed, and only the volume can change. This implies $C_p = \infty$ for all extensive IQG.

When the internal energy (5) is not a *linear* function of the empirical temperature *alone*, the gas and absolute temperature scales do not coincide. For an ICG, the constant of proportionality between the internal energy and the empirical temperature is some multiple of the number of particles, N, which is a constant. Rather, for an IQG, the number of particles is variable, being a function of the temperature.

The only thing that the zeroth law demands is that the empirical temperature be the same when two systems arrive in a state of mutual thermal equilibrium. Once the empirical scale has been chosen, the absolute temperature must be a monotonically increasing function of it, say $T(t) = t^r$ for r > 0.

In order to render the increment in the heat,

$$dQ = dU + p dV$$

$$= \alpha t^r z^{\alpha - r} d \log z = \alpha V^{-r/(q-r)} z^{\alpha} d \log z,$$
(10)

a perfect differential, we may either divide through by t^r to obtain

$$\frac{\alpha}{\alpha - r} d\left(t^{\alpha - r} V^{(\alpha - r)/(q - r)}\right) = \frac{dQ}{t^r} =: dS, \tag{11}$$

or multiply through by $V^{r/(q-r)}$ to get

$$d\left(t^{\alpha}V^{\alpha/(q-r)}\right) = V^{r/(q-r)}dQ =: dZ. \tag{12}$$

The potential (4) is a higher power of z than the entropy,

$$S = \frac{\alpha}{\alpha - r} z^{\alpha - r} = \frac{\alpha}{\alpha - r} t^{\alpha - r} V^{(\alpha - r)/(q - r)}, \qquad (13)$$

which becomes extensive when $\alpha = q$. Since

$$H = U + pV = \frac{q}{q - r} t^{\alpha} V^{(\alpha - r)/(q - r)}, \qquad (14)$$

the difference between (14) and t^r times (13),

$$G = U + pV - t^r S = \left(\frac{q}{r} - \frac{\alpha}{r} \frac{q - r}{\alpha - r}\right) pV, \tag{15}$$

shows that the Gibbs free energy, G, is a measure of the degree of nonextensivity. It is well known that (9) diverges when the chemical potential is identically zero [10, p. 229]. This occurs for an extensive IQG.

For a nonrelativistic IQG, irrespective of whether it obeys Bose or Fermi statistics, $\alpha=q,\,q/r=\frac{5}{2}$, and we shall set r=1 in order to make the comparison with conventional formulas as close as possible. Apart from constant factors, $U=T^{5/2}V$, and $Z=V^{2/3}U=T^{5/2}V^{5/3}$. Since the latter must be a power of $z=TV^{2/3}$ only, U cannot contain any arbitrary constants. Conventionally, such an arbitrary constant is identified with the chemical

potential at absolute zero. Since conventional IQG are extensive, the chemical potential vanishes identically on account of (15).

In an adiabatic process, the entropy $S=\frac{5}{3}z^{3/2}=\frac{5}{3}T^{3/2}V$, and the potential, $Z=z^{5/2}=\frac{3}{2}pV^{5/3}$, are constant. The pressure, $p=\frac{2}{3}T^{5/2}$, is independent of the volume, and satisfies the homogeneity condition, (3).

A new adiabatically conserved potential, (4), has appeared, for which the cell size, $R = V^{1/(q-r)}$, raised to the power r, is the integrating factor for the heat,

$$R^r dQ = dZ$$
,

which puts it on par with that of the second law, (11). Since both (4) and (13) are constant for adiabatic processes, they provide no criterion for the accessibility of states under adiabatic transitions. For processes of pure heat conduction, U- and Z-conservation equilibrations give the greatest mean temperature possible, and the evolution is determined by the second law, because the power means are monotonic increasing functions of their order. However, for processes involving pure deformations, U- and Z-conservation equilibriations will not be equivalent.

Consider a system comprised of n cells, adiabiatically isolated from the environment. Initially the walls of the cells are rigid and adiabatic. When the walls are replaced by deformable, diathermal ones, there will be probabilities, p_i that the cells will have linear dimensions, R_i and temperatures, t_i . Probabilities enter naturally when dealing with processes of heat exchange: Heat is the uncontrollable form of work [11], and temperature is its measure.

Carathéodory's principle says that states arbitrarily near to one another may be adiabatically inaccessible; it does not say what those states are. This must come from an additional assumption that only those states that are adiabatically accessible from a given state are those for which the internal energy increases [12],

$$\overline{\Delta U} = -\frac{r}{q - r} z^{\alpha} \sum_{i=1}^{n} p_{i} \int_{V_{i}}^{V_{f}} V^{-q/(q - r)} dV$$

$$= z^{\alpha} \left\{ V_{f}^{-r/(q - r)} - \sum_{i=1}^{n} p_{i} V_{i}^{-r/(q - r)} \right\}$$

$$= \text{const.} \times \left\{ t_{f}^{r} - \sum_{i=1}^{n} p_{i} t_{i}^{r} \right\} \ge 0, \tag{16}$$

by the work that must be done. The last line follows from the condition of adiabaticity, $z = tV^{1/(q-r)} = \text{const.}$ Inequality (16) asserts that adiabatic transitions to neighboring states are possible so long as the final temperature is greater than the mean temperature, $t(r) = (\sum_{i=1}^{n} p_i t_i^r)^{1/r}$.

This is tantamount to requiring the final mean volume to be greater than $\left(\sum_{i=1}^{n} p_i V_i^{-r/(q-r)}\right)^{-(q-r)/r}$. In

an adiabatic, energy-conserving equilibration, the final mean volume,

$$V_f = \left(\sum_{i=1}^n p_i V_i^{-r/(q-r)}\right)^{-(q-r)/r} \to V_{\min},$$

in the limit as $q \to r$, where V_{\min} is the smallest cell volume. The final mean volume, V_f , is a decreasing function of its order. On account of the adiabatic constraint, the mean temperature is the highest mean temperature, t(q). The smaller the difference, q-r, the more weight is given to smaller cell volumes.

Alternatively, if no work is performed, the average change in the internal energy cannot increase,

$$\overline{\Delta U} = V^{\alpha-r)/(q-r)} \sum_{i=1}^{n} p_i \int_{t_i}^{t_f} dt^{\alpha}$$

$$= V^{(\alpha-r)/(q-r)} \left\{ t_f^{\alpha} - \sum_{i=1}^{n} p_i t_i^{\alpha} \right\} \le 0, \quad (17)$$

in a process involving only pure thermal conduction. This says that the final common mean temperature of the cells cannot be greater than the mean temperature, $t(\alpha)$, which is the greatest mean temperature in nonextensive systems with $\alpha>q$. Inequality (17) can be related to Jensen's inequality, and constitutes a criterion for spontaneous transition [13]. Consequently, $\overline{\Delta U}=0$ coincides with $\overline{\Delta Z}=0$ for processes in which no work is done, where the highest final mean temperature is reached.

Contrarily, the largest mean volume coincides with the largest cell volume, $V_{\rm max}$, in an isothermal energy-conserving equilibration in the same limit as $q \downarrow r$. The energy equilibriating conservation condition for an isothermal process gives the final mean volume

$$V_f = \left(\sum_{i=1}^n p_i V_i^{(\alpha-r)/(q-r)}\right)^{(q-r)/(\alpha-r)} \to V_{\text{max}} \quad (18)$$

in the limit as $q \to r$ if $\alpha > q$. The final volume is now an increasing function of its order. The larger the order, the more weight is given to larger cell volumes V_i .

The final mean volume in a Z-conserving equilibration,

$$V_f = \left(\sum_{i=1}^n p_i V_i^{\alpha/(q-r)}\right)^{(q-r)/\alpha},$$

will be greater than in a *U*-conserving equilibration, (18), but will tend to the same value, V_{max} , in the limit as $q \downarrow r$.

The limit $q\downarrow r$ will be shown to be the transition from an IQG to an ICG in nonextensive systems with $\alpha>q$, or extensive systems in general. In that limit, an adiabatic transition corresponds to the smallest volume, while an isothermal transition corresponds to the greatest final volume. Hence, adiabatic to isothermal changes cover the

entire spectrum of mean values of the volume, analogous to a polytrope, where adiabats and isotherms correspond to zero and infinite heat capacities, respectively.

If the temperatures and sizes of the cells are similarly ordered, so that cells of higher temperatures have larger sizes, in compliance with Charles' law,

$$z(q) = \left(\sum_{i=1}^{n} p_{i} t_{i}^{q} R_{i}^{q}\right)^{1/q} > t(q) R(q)$$

$$= \left(\sum_{i=1}^{n} p_{i} t_{i}^{q}\right)^{1/q} \left(\sum_{i=1}^{n} p_{i} R_{i}^{q}\right)^{1/q}, \quad (19)$$

unless all the temperatures, t_i , and cell sizes, R_i , are equal. If there is some constraint that makes the temperatures decreasing functions of the cell sizes, then the discrete analog of Čhebyshev's inequality, (19), is reversed [1, pp. 43–44].

It therefore follows that the terms in the hierarchy

$$z_h > z(q) > z(q-r) > z(r) > z_c,$$

are greater than the corresponding terms in the hierarchy

$$t_h R_{\text{max}} > t(q)R(q) > t(q-r)R(q-r) > t(r)R(r) > t_c R_{\text{min}}$$

This is implied by the hierarchy

$$t_h > t(q) > t(q-r) > t(r) > t_c$$

in the case of pure thermal conduction, or, in the case of an isothermal process by

$$R_{\text{max}} > R(q) > R(q-r) > R(r) > R_{\text{min}}$$

where R_{max} and R_{min} are the largest and smallest cell lengths, respectively.

In a Z-equilibrating conservation,

$$\overline{\Delta Z} = \sum_{i=1}^{n} p_i \int_{z_i}^{z_f} dZ(z) = z_f^{\alpha} - \sum_{i=1}^{n} p_i z_i^{\alpha} = 0, \quad (20)$$

imposing $z_f = z(\alpha)$. The fact that power means are monotonically increasing functions of their order,

$$\left(\sum_{i=1}^{n} p_i z_i^{\alpha}\right)^{1/\alpha} > \left(\sum_{i=1}^{n} p_i z_i^{\alpha-r}\right)^{1/(\alpha-r)},$$

for $\alpha > r$, guarantees the second law

$$\overline{\Delta S} = \sum_{i=1}^{n} p_i \int_{z_i}^{z_f} \frac{dZ(z)}{z^r}$$

$$= \frac{\alpha}{\alpha - r} \left\{ z^{\alpha - r}(\alpha) - \sum_{i=1}^{n} p_i z_i^{\alpha - r} \right\} \ge 0. \quad (21)$$

This can be considered the essence of the second law for power means [3].

The transition between IQG and ICG is usually considered to take place in the high temperature limit. Here, we show that the transition takes place in the limit as $\alpha \downarrow r$. In this limit (21) becomes indeterminate, of the form 0/0. Invoking l'Hôpital's rule, we get

$$\overline{\Delta S} = \log \left(\sum_{i=1}^{n} p_i z_i^r \right) - r \sum_{i=1}^{n} p_i \log z_i.$$
 (22)

It is important to observe that the limit $q \downarrow r$ cannot be taken since it would leave the cell sizes R_i undefined.

Rather, if we consider an extensive system, where $\alpha=q,$ and consider only isochoric processes, then (21) becomes

$$\overline{\Delta s} = \frac{q}{q-r} \left\{ \left(\sum_{i=1}^{n} p_i t_i^q \right)^{(q-r)/q} - \sum_{i=1}^{n} p_i t_i^{q-r} \right\},\,$$

upon dividing through by the constant volume, V, where s is the entropy density. Now, taking the limit as $q \downarrow r$, and employing l'Hôpital's rule we get

$$\lim_{q\downarrow r} \overline{\Delta s} = r \log \left[\frac{t(r)}{t(0)} \right] = \log \left[\frac{u(1)}{u(0)} \right] > 0.$$

The quantities $u(1) = \sum_{i=1}^{n} p_i u_i$, and $u(0) = \prod_{i=1}^{n} u_i^{p_i}$ are now to be interpreted as *molar* energies, and not as *densities* [14]. The second law inequality now follows from the arithmetic-geometric mean inequality [7], implying that the maximum amount of work has been done in going from the initial state, characterized by the mean energy, u(1), to the final state, with energy u(0).

The ICG limit also allows a connection to be made with multifractals and information theory [15], in the isothermal processes occurring in nonextensive systems. In this case, (22) becomes

$$\overline{\Delta S} = \log \left(\sum_{i=1}^{n} p_i R_i^{D\tau} \right) - D\tau \sum_{i=1}^{n} p_i \log R_i, \qquad (23)$$

where we have set the exponent, $r = D\tau$. The exponent D is the Hausdorff dimension, defined as

$$\sum_{i=1}^{n} R_i^D = 1. (24)$$

Condition (24) plays a role analogous to the Kraft (in)equality for a uniquely decipherable code.

If we consider the exponent, $\tau < 1$, then we can apply Hölder's inequality in the reverse form [1, p.25]

$$\left[\sum_{i=1}^{n} \left(p_i^{1/\tau} R_i^D\right)^{\tau}\right]^{1/\tau} \left[\sum_{i=1}^{n} p_i^{-(1/\tau) \cdot \tau/(\tau - 1)}\right]^{(\tau - 1)/\tau} \\ \leq \sum_{i=1}^{n} R_i^D = 1,$$

on the strength of (24). Setting $\tau = (\alpha - 1)/\alpha < 1$, with $\alpha > 1$, Hölder's inequality becomes

$$\sum_{i=1}^{n} p_i R_i^{D\tau} \le \left(\sum_{i=1}^{n} p_i^{\alpha}\right)^{1/\alpha}.$$
 (25)

It is easy to see that we have equality in (25) if

$$R_i^D = \frac{p_i^\alpha}{\sum_{i=1}^n p_i^\alpha},$$

or

$$D\log R_i = \alpha \log p_i - \log \sum_{i=1}^n p_i^{\alpha}, \tag{26}$$

which also satisfies the definition of the Hausdorff dimension, (24). Multiplying (26) through by p_i , summing, and introducing the result into (23) give

$$\overline{\Delta S} = (\alpha - 1)(S_1 - S_\alpha) > 0, \tag{27}$$

where S_1 and S_{α} are the Shannon,

$$S_1 = -\sum_{i=1}^n p_i \log p_i,$$

and Rényi,

$$S_{\alpha} = \frac{1}{1 - \alpha} \log \sum_{i=1}^{n} p_i^{\alpha},$$

entropies of order 1 and α , respectively. The inequality in (27) is due to the fact that for $\alpha>1$ the Shannon entropy is greater than the Rényi entropy, while, for $\alpha<1$, the converse is true. Hence, the second law (27) is always satisfied. Moreover, in the limit as $\alpha\to1$, l'Hôpital rule shows that

$$S_1 = \lim_{\alpha \to 1} S_\alpha = -\sum_{i=1}^n p_i \log p_i.$$

In this limit, the average entropy difference, (27), vanishes.

Hence, (27) shows that in the limit of an isothermal ICG, the average entropy difference is always proportional to the absolute value of the difference between the Shannon and Rényi entropies, when D is identified as the Hausdorff dimension.

The generalization of the Hausdorff dimension to multifractals, where the generator of cell sizes of lengths R_i with probabilities, p_i , require two exponents [16],

$$\sum_{i=1}^{n} p_i^{\alpha} R_i^{D_{\alpha}(1-\alpha)} = 1, \tag{28}$$

where D_{α} is supposed to be some generalization of the Hausdorff dimension, D.

If $\{p_i\}$ is a complete distribution, and α is restricted to the open interval (0,1) in order ensure that the Rényi entropy be concave, then the usual Hölder inequality, and condition (28), give

$$\sum_{i=1}^{n} R_i^{D_{\alpha}} \ge 1. \tag{29}$$

Since for $\alpha = 1$, (26) becomes

$$D_1 = \frac{S_1}{\sum_{i=1}^n p_i \log(1/R_i)},$$

it was thought [16] that D_{α} should be related to the Rényi entropy in a similar form, viz.,

$$D_{\alpha} = \frac{S_{\alpha}}{\sum_{i=1}^{n} p_i \log(1/R_i)}.$$

This can be obtained by averaging

$$D_{\alpha}(1-\alpha)\log R_i = -\log \sum_{i=1}^n p_i^{\alpha}.$$
 (30)

Exponentiating both sides, multiplying by p_i^{α} , and summing does give (28). But, since the right side of (30) is independent of the index i, so too must be the left side. This means that all the cell sizes have the same length

$$R^{D_{\alpha}} = \left(\sum_{i=1}^{n} p_i^{\alpha}\right)^{-1/(1-\alpha)} = e^{-S_{\alpha}}.$$

In view of condition (29), this would imply

$$S_0 \geq S_{\alpha}$$

showing that equal probabilities maximize the entropy: The greatest entropy is the Hartley entropy, $S_0 = \log n$, which is frequency independent.

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